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Active Sites of Solid Acidic Catalysts

III. Infrared Study of the Water Gas Conversion Reaction on Alumina[1]

Y. AMENOMIYA

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR9

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The water gas conversion reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$) on alumina was investigated by infrared spectroscopy over a temperature range between 200 and 600°C, following the kinetic study reported as Part II of this series. ir spectra were recorded during the reaction which proceeded unidirectionally at a steady rate. Thus formate ion was found on the surface in both forward and backward reactions. The results also showed that the concentration of the surface formate ion responded quickly to the change of the reactant pressure and that the rates of the decomposition of the surface formate were in reasonable agreement with those of the overall reaction at the same surface coverage. It was therefore concluded that the surface formate ion found in this study is the intermediate of the water gas conversion reaction on alumina. Some formate ions, however, are so strongly held on the surface that they do not participate in the reaction below 500°C. Although the rate-determining step of the $CO_2 + H_2$ reaction is the decomposition of the surface formate ion in the absence of water, the rate-determining step is shifted to the formation of formate ion in the presence of water.

INTRODUCTION

In the previous paper (*1*), the kinetics of the water gas conversion reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$) was studied on alumina, and the reaction rates (molecules sec^{-1} cm^{-2}) in respective directions were obtained as

$$r_1(CO_2 + H_2) = 5.07 \times 10^{13} \times \exp(-16100/RT)p_d{}^{\frac{1}{2}}p_h{}^{\frac{1}{2}} \quad (1)$$

$$r_2(CO + H_2O) = 7.51 \times 10^{14} \times \exp(-22900/RT)p_m \quad (2)$$

where p_d, p_h, and p_m are the partial pressures (Torr) of carbon dioxide, hydrogen, and carbon monoxide, respectively. In this report the same reaction has been investigated by infrared spectroscopy in order to obtain further information on the mechanism of the water gas reaction on alumina. The infrared spectroscopic technique has been used in the studies of the water gas reaction on zinc oxide and magnesia, and formate ion was detected as the intermediate of the reaction (*2–4*). On alumina, however, investigations have been rather focused on the decomposition of formic acid (*2, 5, 6*).

Most of the infrared spectroscopy in the present study was carried out while the reaction was proceeding in a steady state in order to detect surface species related to the reaction. The reaction conditions were similar to those employed in the previous work, namely, the reactant pressures up to 500 Torr (1 Torr = 133.3 Nm^{-2}) and the reaction temperature between 200 and 600°C. Special attention

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was paid to the identification of the reaction intermediate, because the spectroscopy of catalyst surface could detect adsorbed species which was not involved in the direct reaction path. Two types of side reactions are possible to form such surface species:

$$\begin{tikzcd} A \arrow[r, shift left] \arrow[d, shift left] & I \arrow[l, shift left] \arrow[r, shift left] & B \arrow[l, shift left] \arrow[d, shift left] \\ S_1 \arrow[u, shift left] & & S_2 \arrow[u, shift left] \end{tikzcd} \qquad \begin{tikzcd} A \arrow[r, shift left] & I \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & B \arrow[l, shift left] \\ & S \arrow[u, shift left] & \end{tikzcd}$$

(I) (II)

in which I is the intermediate of reaction A → B, and S is the product of side reaction. The possibility of the above cases is discussed with the experimental results obtained in the present work.

EXPERIMENTAL METHODS

Materials. Alumina used in this study was taken from the same batch of Alon alumina (Cabot Corp., Boston, Mass.) used in the previous work (*1*). An amount of 120 mg of the Alon was pressed into a disk of 19-mm diameter. The total surface area of the disk was 1.10×10^5 cm^2. The treatment of catalyst and the gases used were described previously (*1*).

Apparatus and procedure. The apparatus used for the present study has been described in detail elsewhere (*7*). It was a closed circulation system incorporated with a high temperature infrared cell. The system was constructed with stainless-steel bellows valves and a bellows circulation pump, and the cell was made of quartz, with UHV flanges. The volume of the system including the cell was about 720 ml. The temperature of the catalyst disk in the cell was controlled between room temperature and 700°C by a programmable temperature controller. The system was connected through valves to a high vacuum line equipped with a mass spectrometer, so that the analysis of the gas phase during reaction and the temperature-programmed desorption of adsorbed species after reaction could be carried out when necessary. The whole system could be evacuated to a routine vacuum of 10^{-8} Torr.

ir spectra were recorded with a Beckman ir 4230 spectrophotometer at a scanning speed of 150 cm^{-1}/min and a spectral slit width of 3 cm^{-1}. The internal chopper of the spectrophotometer was disengaged and an auxiliary chopper was installed between the cell and the light source to minimize the disturbance due to the emission from the heated catalyst. All spectra were recorded in the linear absorbance scale.

Each direction of the water gas reaction was studied separately as was done previously (*1*): The mixture of carbon dioxide and hydrogen was circulated through the cell and a trap cooled by a dry ice–alcohol bath; and carbon monoxide was circulated through the cell and the trap in which triple-distilled water was kept at selected temperatures between 0 and 23°C. Very little product was formed during the reaction on the present catalyst (120 mg), and, moreover, water was trapped during the $CO_2 + H_2$ reaction. Therefore, the backward reaction could be ignored in either reaction.

RESULTS AND DISCUSSION

1. *ir Spectra during Reaction*

Figure 1 shows some typical spectra recorded during a $CO_2 + H_2$ reaction at 400°C. Carbon dioxide was first admitted to the cell (spectrum 1), and the reaction was started by mixing hydrogen by the circulation pump (spectra 2–4). It is seen in the figure that most of the absorption bands due to CO_2 except for a broad band at 1400–1500 cm^{-1} were replaced by two new strong bands at 1590 and 1395 cm^{-1} formed by the reaction. Also a weak band at 2914 cm^{-1} and a still weaker one at 2993 cm^{-1} appeared along with the above two bands. The absorbance of the four bands varied in a constant ratio indicating that all these bands belonged to the same species. The frequencies of the bands (2993, 2914, 1590, and 1395 cm^{-1}) were in good agreement with those of formic acid adsorbed on the same catalyst (2996, 2901, 1592, and 1395 cm^{-1}) and with those found by previous authors with formate ion on alumina (*2, 5, 6, 8*). They also agree reasonably well with the absorption bands of aluminum formate (*9*). Apparently, formate ions were formed on the surface from carbon dioxide and hydrogen.

The reaction of $CO + H_2O$ produced similar spectrum to those in Fig. 1 at temperatures between 400 and 600°C, but the 1395 cm^{-1} band split clearly in two, 1395 and 1380 cm^{-1}. In agreement with the previous authors (*2, 6, 8*), the 2914 and 1590 cm^{-1} bands are assigned to the C–H stretching (ν_1) and O–C–O antisymmetric stretching (ν_4) vibrations, respectively. The 1395 and 1380 cm^{-1} bands are probably due to the O–C–O symmetric stretching (ν_2) and O–C–H in plane bending (ν_5) vibrations, respectively, while the 2993 cm^{-1} band would be ascribable to $\nu_3 + \nu_4$ according to Maas (*10*). Since the same formate ion was observed in both directions of the reaction, the possibility that this surface species is one of the Type I by-products defined in the Introduction can be excluded.

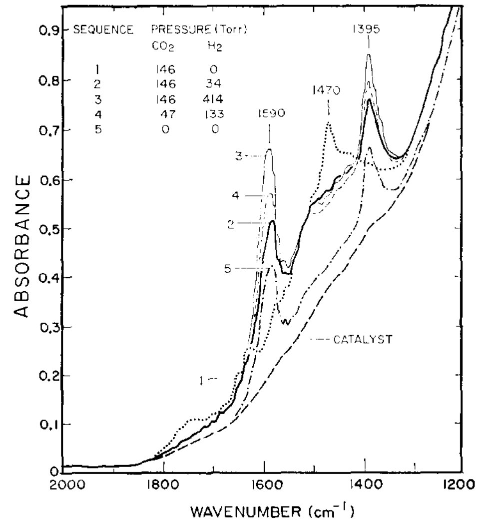

FIG. 1. ir spectra during the reaction $CO_2 + H_2$ at 400°C. The sequence of experiments and the reaction conditions are indicated in the figure. Spectrum 5 was obtained after evacuating the cell for 15 min at 400°C.

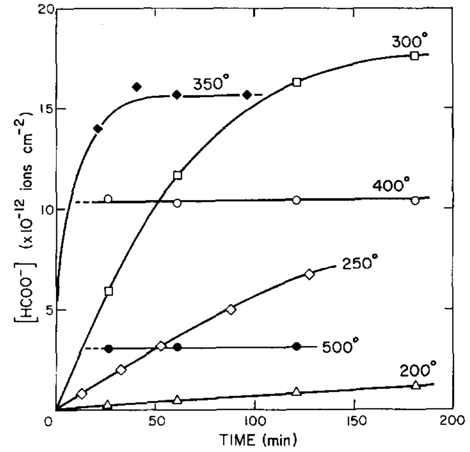

FIG. 2. Time course of the formation of formate ion from $CO_2 + H_2$. All reactions were carried out with 145 Torr of CO_2 and 150 Torr of H_2.

As already reported (*7*), a good linear plot was obtained between the amount of surface formate and the absorbance of the 1590 cm^{-1} band. In this report all surface concentrations of formate ion were calculated from the absorbance of the 1590 cm^{-1} band by the above straight line. The time course of the formation of formate ions thus obtained is shown in Fig. 2. The rate of formation increased with temperature, and above 400°C the surface concentration of the formate became constant in a few minutes, as seen in the figure. The activation energy of the formation of formate was obtained as 20.0 kcal/mole between 200 and 300°C.

At temperatures higher than 400°C, the concentration of the surface formate responded quickly to the change of the reactant pressure as shown in Fig. 1. The intensity of all bands became stabilized within several minutes at each set of pressures. When the gas was pumped out, however, some formate ions remained ad-

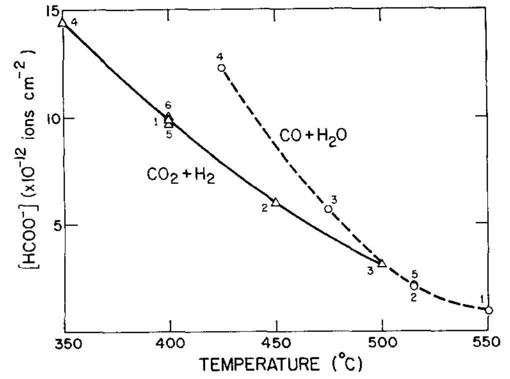

FIG. 3. Temperature dependence of the formate concentration. Number on the points is the sequence of the experiment. Point 6 on the $CO_2 + H_2$ curve was obtained by reheating the catalyst at 400°C after leaving with the gas at room temperature for 16 hr after point 5.

sorbed as shown by spectrum 5 in Fig. 1. This will be discussed later in more detail. The fast response of the formate concentration to the pressures of the reactants was also observed in the $CO + H_2O$ reaction.

Figure 3 demonstrates that the formate concentration in both reactions was quite reproducible after the temperature was varied over a wide range. This reproducibility and the fast response to the change of the reactant pressure both suggest that the surface formate ions are in equilibrium with the reactants in either reaction.

2. Reaction Intermediate

Although the amount of the present catalyst was too small to measure the reaction rate accurately at low temperatures, the rates measured manometrically at 600°C were in good agreement with those measured in the previous study (*1*). For example, the rate of a $CO_2 + H_2$ reaction at 600°C measured in the present system was 4.9×10^{17} molecules sec^{-1} g^{-1}, while the rate obtained previously under similar conditions was 4.3×10^{17} molecules sec^{-1} g^{-1}. Therefore, all reaction rates reported in this paper were calculated by Eq. (1) or (2).

In Fig. 4 the rates thus obtained by varying the pressures of the reactants over a wide range were plotted against the surface concentration of formate ions measured during the reactions spectroscopically. Under the conditions used in these experiments, the reactions virtually proceeded unidirectionally at a steady rate as already pointed out. As seen in Fig. 4, the reaction rate increases linearly with the formate concentration, but it does not go through the origin at low temperatures. The intercept on the abscissa decreases with increasing temperature, while at the same temperature (475°C) the reactions from $CO_2 + H_2$ and $CO + H_2O$ both give the same intercept. These results suggest that the reactions take place through formate ion but a part of the formate ions is adsorbed so strongly (stable) that they do not participate in the reactions. In addition to the results of Fig. 4 the quick response of the formate concentration to the reactant pressure also supports that the formate ion is the intermediate of the water gas conversion on alumina. However, the possibility that the formate ion is a Type II by-product instead of the true intermediate cannot be excluded unless the actual rate of decomposition of formate ions is shown to be equal to the rate of

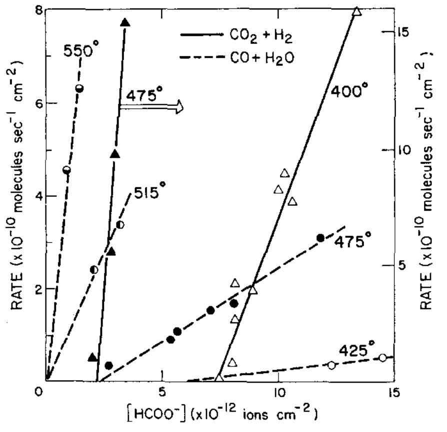

FIG. 4. Reaction rate vs surface concentration of formate ion.

overall reaction. This criticism is valid except for a rare case in which the equilibrium constant of $I \rightleftarrows S$ happens to be unity.

Noto *et al.* (*6*) reported in their study of the decomposition of formic acid on alumina that the decomposition rate of formate ion on the catalyst surface was much slower in vacuum than the rate in the presence of formic acid vapor. In the present study too, the decrease in formate ions by evacuation after a $CO_2 + H_2$ reaction was slow as shown by the upper curve in Fig. 5. When hydrogen was allowed to keep circulating after the reaction by condensing carbon dioxide, however, the formate ions decreased much more rapidly (the lower curve in Fig. 5). Since the same results were obtained by replacing hydrogen by helium as seen in the figure, hydrogen had no chemical effect and the slow rate of decomposition in vacuum must have resulted from a poor thermal conductivity in the evacuated cell. In any case the formate ions on the surface decomposed almost exclusively to CO and H_2O without desorbing as formic acid or CO_2.

The rate of the decomposition of the surface formate ion was measured from the slope on the lower curve of Fig. 5 at various surface coverages and compared in Table 1 with the rate of overall $CO_2 + H_2$ reaction obtained from Fig. 4 at the same temperature and surface coverage. Both rates are in reasonable agreement. It is therefore concluded that the formate ion detected in the present study is the intermediate of the water gas conversion reaction on alumina. Since those formate ions are in equilibrium with the reactants as already discussed, the rate-determining step should be the decomposition of the formate ion either to $CO + H_2O$ or $CO_2 + H_2$ depending on the direction of the reaction.

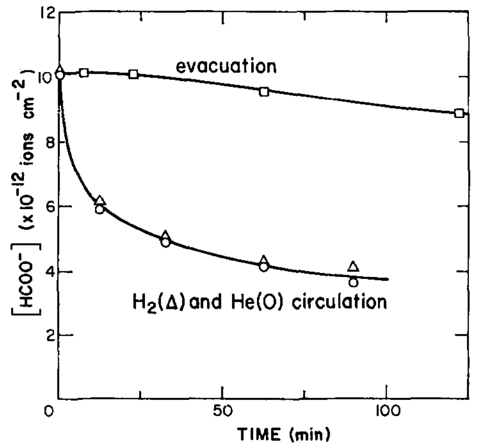

FIG. 5. Decomposition of surface formate ions at 400°C.

TABLE 1

Comparison of the Decomposition Rate of the Surface Formate Ion with the Rate of Overall $CO_2 + H_2$ Reaction at 400°C

$[HCOO^-]$ (ions cm^{-2})	$-d[HCOO^-]/dt$ (ions $cm^{-2}\ sec^{-1}$)	rate ($CO_2 + H_2$) (molecules $cm^{-2}\ sec^{-1}$)
1×10^{13}	3.9×10^{10}	3.5×10^{10}
9×10^{12}	2.1×10^{10}	2.2×10^{10}
8×10^{12}	9.7×10^{9}	8.5×10^{9}

Figure 5 also shows that the decomposition rate became extremely low while some formate ions were still remaining. This is consistent with the results of Fig. 4 that a part of the formate ions was not involved in the reaction at low temperatures.

3. *Effect of Water on Reaction*

As described earlier, the results of Fig. 1 shows that most of the bands due to chemisorbed carbon dioxide disappeared when the reaction took place with hydrogen, that is, the chemisorbed carbon dioxide was displaced either by hydrogen or by formate ions produced. After the catalyst was evacuated (spectrum 5 in Fig. 1), carbon dioxide was readmitted at 150 Torr at 400°C but no bands due to carbon dioxide were observed except for a broad band at 1400–1500 cm^{-1}. Apparently, carbon dioxide was displaced by formate ions. This view is further sup-

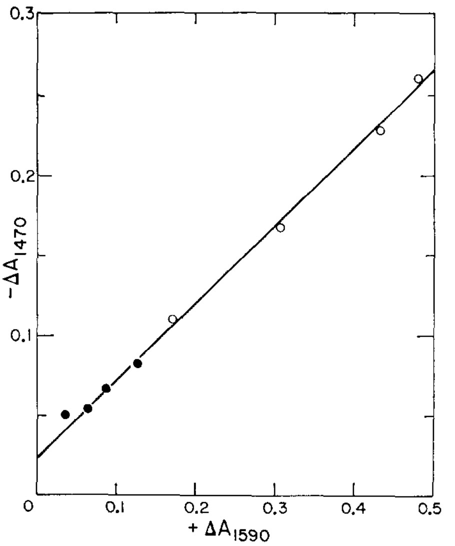

Fig. 6. Absorbance decrease of the 1470 cm^{-1} band as a function of the absorbance increase of the 1590 cm^{-1} band during the $CO_2 + H_2$ reaction at 250°C (●) and 300°C (○).

ported by the results shown by Fig. 6 that the absorbance of the 1470 cm^{-1} band due to chemisorbed carbon dioxide decreased linearly with the formation of the surface formate ions.

The present Alon alumina, when treated at 600°C, gave four absorption bands due to the surface hydroxyl (deuteroxyl) groups at 3804 (2797), 3786 (2782), 3738 (2745), and 3685 (2713) cm^{-1}. The two highest frequency bands correspond respectively to A- and D-bands defined by Peri (*11*), the 3738 cm^{-1} band to either B- or E-band, and the lowest frequency band would probably correspond to C-band. During the $CO + H_2O$ reaction, two more bands appeared at 3590 and 3470 cm^{-1} with some increase in the 3738 and 3685 cm^{-1} bands. The two highest frequency bands remained almost unchanged. The new bands which were broad and strong are apparently due to hydrogen-bonded hydroxyl groups formed by the adsorption of water. When the catalyst was not evacuated thoroughly, the admission of dry carbon monoxide in the cell produced formate ions on the surface. However, the intensities of the isolated surface hydroxyl groups (3804–3685 cm^{-1}) on this slightly wet catalyst were almost the same as those on well-evaluated catalyst which did not produce the surface formate at all with dry carbon monoxide. The isolated hydroxyl groups do not seem to be directly responsible for the formation of formate ions.

Although little change in hydroxyl groups was observed during the $CO_2 + H_2$ reaction with the trap at dry ice–alcohol temperature, the presence of water vapor retarded the reaction seriously as reported previously (*1*). For example, water vapor at 22 Torr stopped the reaction at 400°C almost completely. When carbon dioxide and hydrogen were reacted at 400°C with 20 Torr of water vapor in the present study, only a trace of formate ions was detected with no sign of carbon dioxide chemisorption. Therefore, water retards the reaction by blocking the formation of the surface formate (by blocking the chemisorption of carbon dioxide) but not

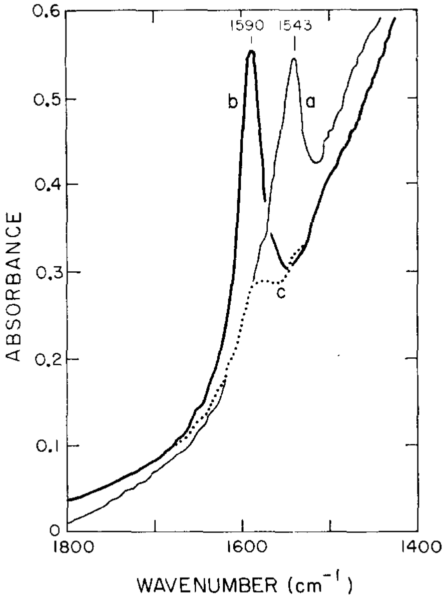

Fig. 7. ir spectra with $^{13}CO_2$. (a) $^{13}CO_2 + H_2$ at 400°C; (b) $^{13}CO_2 + H_2 + {}^{12}CO + H_2O$ at 400°C; (c) the same as (b) but at 500°C.

by blocking the decomposition of formate ions.

In another experiment, a reaction was started with a mixture of $^{13}CO_2 + H_2$ at 400°C. A part of the resultant spectrum is shown by spectrum a in Fig. 7 in which the O–^{13}C–O antisymmetric stretching vibration was observed at 1543 cm^{-1}. After the spectrum was recorded, ^{12}CO and water vapor were added to the reaction system in such a ratio that the value $[CO][H_2O]/[CO_2][H_2]$ was slightly smaller than the equilibrium constant at 400°C (0.0809). The 1543 cm^{-1} band immediately shifted to 1590 cm^{-1} as shown by spectrum b in Fig. 7 indicating that almost all $H^{13}CO_2^-$ was wiped out probably by water and $H^{12}CO_2^-$ was formed from carbon monoxide. The mass spectrometric analysis of the gas phase showed very little change in the isotopic composition in both carbon dioxide and carbon monoxide as expected from Eqs. (1) and (2). The temperature was then raised to 500°C and spectrum c in Fig. 7 was recorded. The isotopic composition of the surface formate was calculated roughly from the spectrum as 95% $H^{12}CO_2^-$ and 5% $H^{13}CO_2^-$, while the mass spectrometric analysis showed that the atom fraction of ^{13}C in the carbon monoxide was 3% and that in the carbon dioxide was 78%. Therefore, the surface formate ions are still in equilibrium with $CO + H_2O$ but not with $CO_2 + H_2$. As soon as the water was trapped briefly, the 1543 cm^{-1} band became stronger at the sacrifice of the 1590 cm^{-1} band. Finally the temperature was increased to 600°C for 90 min, and the increase in ^{12}C in the carbon dioxide indicated that a total of 120 μmole of carbon monoxide was converted to carbon dioxide. This amount was in good agreement with 115 μmole calculated by Eq. (2) as the total amount of carbon monoxide reacted. It was found recently that the direct exchange of carbon, $^{13}CO_2 + {}^{12}CO \rightleftharpoons {}^{12}CO_2 + {}^{13}CO$, did not take place on alumina at least up to 400°C (*12*).

It was discussed in the previous report (*1*) that r_1 calculated from Eq. (*1*) at an equilibrium composition was much larger than r_2 and that the real r_1 in the presence of water would be much smaller than expressed by Eq. (1). This has been indeed proved by the above results which also shows that, in the presence of water, the rate-determining step of r_1 shifts to the formation of the surface formate ions,

$$CO_2 + H_2 \xleftrightarrow{\wedge} HCOO^-(a) + H^+(a) \rightleftharpoons CO + H_2O.$$

4. Decomposition of Surface Formate Ion

Noto *et al.* (*6*) and Fukuda *et al.* (*13*) studied the decomposition of formic acid on alumina at temperatures below 200°C, and concluded that formate ion observed on the surface by infrared spectroscopy was not a reaction intermediate. The decomposition rate was dependent on the acid pressure in the gas phase and was one to two order of magnitude greater than the rate of the decomposition of the surface formate ions observed in the present work. As concluded in this report, the surface formate ion is the intermediate of the water gas conversion reaction which occurs at a measurable rate on the present alumina at 300°C or higher (*1*). Apparently, the two reactions, the decomposition of formic acid at low temperatures and that of the surface formate ion at high temperatures, take place by different mechanisms.

Since the reaction rates shown in Fig. 4 are the rates of the decomposition of the surface formate ion, the rate constant of the decomposition reaction, $-d[HCOO^-]/dt = k[HCOO^-]$, was obtained from the slope of the straight lines in the figure as

$$k(\rightarrow CO_2 + H_2) = 8.83 \times 10^7 \exp(-35700/RT)\ sec^{-1}$$

$$k(\rightarrow CO + H_2O) = 6.75 \times 10^7 \exp(-29900/RT)\ sec^{-1}.$$

The average life of the formate ion $(1/k)$

at 500°C, for example, is 140 sec for dehydrogenation and 4 sec for dehydration. The results are consistent with those of the temperature-programmed desorption (TPD) of the surface formate reported earlier (*7*), that is, TPD spectrum consisted of mainly carbon monoxide (500–600°C) and water (500°C) peaks but the amount of carbon dioxide desorbed was negligible.

CONCLUSION

(i) The water gas conversion reaction on alumina takes place via formate ion.

(ii) The rate-determining step is the decomposition of the surface formate ion in the $CO + H_2O$ reaction and also in the $CO_2 + H_2$ reaction in the absence of water.

(iii) In the presence of water, however, the rate-determining step of the $CO_2 + H_2$ reaction shifts to the formation of formate ion.

(iv) Carbon dioxide, water, and formate ion share the sites for adsorption.

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REFERENCES

1. Amenomiya, Y., *J. Catal.* **55**, 205 (1978).
2. Scholten, J. J. F., Mars, P., Menon, P. G., and Van Hardeveld, R., *Proc. Int. Congr. Catal., 3rd, 1964* **2**, 881 (1965).
3. Ueno, A., Yamamoto, T., Onishi, T., and Tamaru, K., *Bull. Chem. Soc. Japan* **42**, 3040 (1969).
4. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **66**, 756 (1970).
5. Hirota, K., Kuwata, K., Otaki, T., and Asai, S., *Actes Congr. Int. Catal., 2nd, 1960*, p. 809 (1961).
6. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63**, 2300 (1967).
7. Amenomiya, Y., *Appl. Spectrosc.* **32**, 484 (1978).
8. Greenler, R. G., *J. Chem. Phys.* **37**, 2094 (1962).
9. Donaldson, J. D., Knifton, J. F., and Ross, S. D., *Spectrochim. Acta* **20**, 847 (1964).
10. Maas, J. P. M., *Spectrochim. Acta* **33A**, 761 (1977).
11. Peri, J. B., *J. Phys. Chem.* **69**, 220 (1965).
12. Morikawa, Y., and Amenomiya, Y., *J. Catal.* **54**, 281 (1978).
13. Fukuda, K., Noto, Y., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63**, 3072 (1967).